

Electronic structure of CeCo₂ thin films studied by x-ray absorption spectroscopy^{*}

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Abstract

We present a x-ray absorption near-edge structure study (XANES) at Ce L₃-, and Co K-edges of CeCo₂ thin films with the thickness varying from 30nm to 140nm. The Ce L₃-edge measurements exhibit the mixed valence nature and tetravalent contribution that increases with the thickness of CeCo₂. The variation in the spectral intensity observed at Co K-edge threshold indicates that there is a change in 3d occupancy and also in 3d-4f-5d hybridization. This study shows the effect of surface to bulk ratio and how it influences the charge transfer between Ce and Co ions and hence the electronic structure of CeCo₂ thin films.

Keywords: XANES; Mixed Valence; Surface; Thin Film

1. Introduction

The behavior of 4f electrons in rare-earth compounds possesses both localized and band-like characters. It becomes clear that the electronic and magnetic properties of materials in nanoscale are different from the bulk even though the chemical composition being the same. Recent study on CeAl₂ has demonstrated that the bulk CeAl₂ exhibits magnetic ordering while CeAl₂ nanoparticles show nonmagnetic nature [1]. This phenomena has been attributed to the effect of surface to bulk ratio [2]. On the contrary, CeCo₂ exhibits the opposite behavior [3,4]. It would be of interest to investigate how bulk to surface effect influences the electronic structure on CeCo₂. (Chungli: Can you say something here about 3d occupancy and mixing? Because Al gives no 3d electrons, it would be good to use a few sentence to highlight the importance of the physics. And then XANES is a powerful tool to probe the 3d occupancy etc.) X-ray absorption near edge structure (XANES) is a useful tool to study the core level changes and understand the electronic structure with thin films of different thickness.

2. Experimental

The CeCo₂ thin films of thickness 30, 40, 70, 110 and 140 nm were prepared by flash evaporation of bulk CeCo₂ ingot onto a liquid nitrogen cold trap in a 0.1 torr of high purity helium and the thickness of these films were monitored by a quartz crystal oscillator during the evaporation process. Details are given elsewhere [1]. X-ray absorption measurements were carried out at beamline 17C at the National Synchrotron Radiation Research Center (NSRRC), Taiwan in fluorescence mode at room temperature.

3. Results and discussions

Fig. 1(a) shows XANES spectra at Ce L₃-edges of CeCo₂ thin films. The unoccupied Ce 5d orbital produces two prominent L₃ white lines, marked as A₁ and B₁ which are ascribed respectively to $2p^*4f^1(5d6s)^4$ and $2p^*4f^0(5d6s)^5$ final states, corresponding to Ce³⁺ and Ce⁴⁺ states [5]. The $2p^*$ denotes a hole in 2p level. As evident from the figure, there is a clear spectral evolution indicating the valence change with thickness. The enhancement of $4f^1$ states in very thin films implies the increased 4f electron occupancy of Ce atoms.

XANES spectra at Co K-edge are presented in Fig. 1(b). The absorption feature A₂ at ~ 7110 eV primarily reflects the density of empty 3d states through the s-p-d re-hybridization [6]. The systematic reduction of the feature A₂ with thickness shows the electronic perturbation of the density of state driven resulting from the surface to bulk ratio. The inset of the Fig. 1(b) obtained after subtracting the bulk spectra, shows that the hybridization between conduction states of Ce 4f5d and Co 3d states increases with film thickness. It is also noted that the unoccupied 3d states increase as film thickness decreases. By comparing the results from Ce L₃- and Co K-edges, the charge transfer between Ce and Co induces valence change in Ce due to the different surface to bulk ratio.

4. Conclusions

The XANES study at Ce L₃-edge revealed the mixed valence nature of Ce ions and the contribution of Ce⁴⁺ is reducing as thickness decreases. On the other hand, the XANES at Co K-edge provides evidence that the 3d occupancy varies with film thickness. These results suggest that the valence change is due to the charge transfer driven by the surface to bulk ratio effect.

Acknowledgements

This work was supported by the U.S. Department of Energy, under Contract No. [DE-AC02-05CH11231](#) and the National Science Council of the Republic of China through grant number ?????????????.

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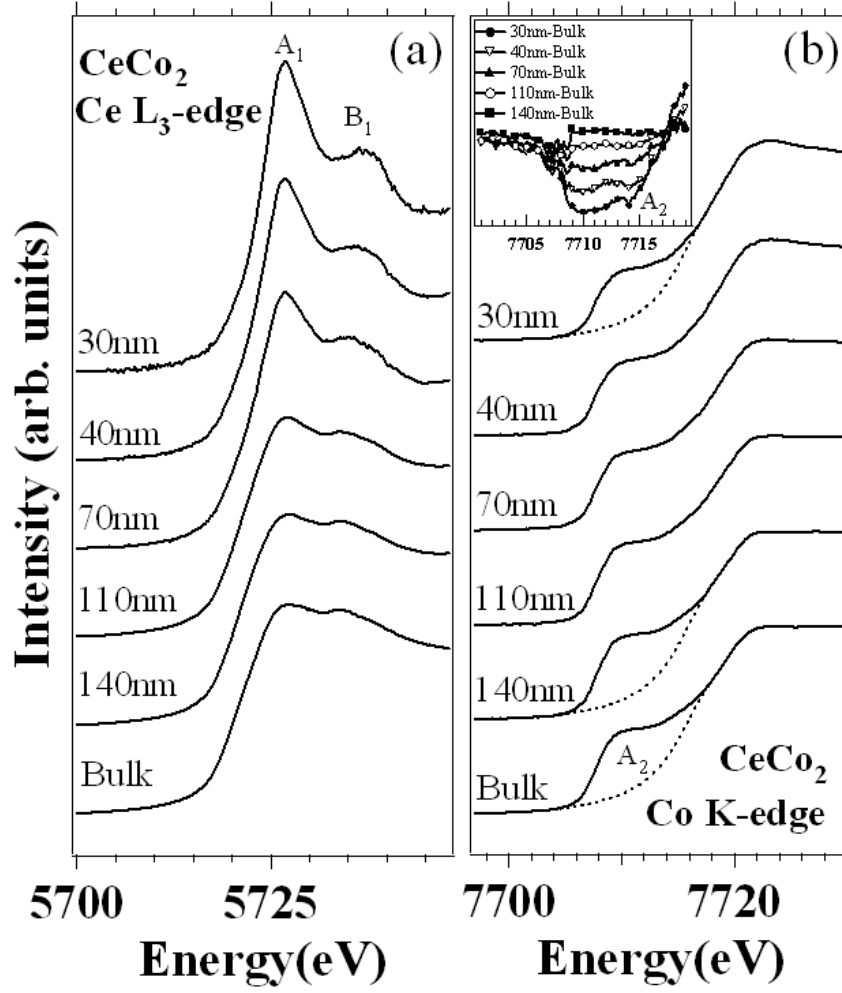


Figure. 1: XANES spectra for bulk CeCo_2 and thin films at (a) Ce L_3 -edge and (b) Co K-edge. Inset in (b) is obtained after subtracting the spectrum of bulk CeCo_2 .